



Determination of Trace Impurities in High-Purity Copper by Sequential ICP-OES with Axial Viewing

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

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Introduction

The determination of trace impurities in high-purity metals and alloys is an important part of the quality-control process in the manufacture of these materials. Trace impurities can have major effects on the properties of the finished products, and in many cases it is desirable to minimize, or at least to be able to control, the levels of certain trace impurities. For example, the level of Ag and S in high-purity Cu wire may be required not to exceed 0.1 parts per million (ppm) [1].

The analysis of antiquities such as bronzes for trace impurities is of interest to archaeologists, and because bronzes consist largely of Cu, the analytical problems will be similar to those encountered with high-purity coppers.

A variety of methods have been used for the analysis of high-purity coppers and of bronzes. The atomic absorption and atomic emission spectrometric methods have both been applied to the analysis of coppers and bronzes for trace impurities [1–6].

Flame atomic absorption spectrometry (FAAS) has been used for the analysis of copper [2,3] but the applicability of this technique is often limited by inadequate detection limits. For example, an impurity present at 1 part per million in solid copper will be reduced to a concentration of 20 parts per billion (ppb) after dissolution and dilution of the Cu to 2% w/v. Since the flame AAS detection limit, even for a sensitive element like Zn, is 2 ppb [7], and the lower limit of quantification is about a factor of 10 above the detection limit, or 20 ppb in this case, it is clear that Zn in a 2% w/v copper solution may not be reliably quantified at levels lower than 1 ppm in the original material. Further, AAS cannot be used for determination of certain non-metals, like sulfur; because the most sensitive lines of such elements often lie in the vacuum ultraviolet region.

Graphite furnace AAS (GFAAS) can be used for measurement of lower levels of trace elements, but suffers the additional limitation, in comparison with FAAS, that certain highly refractory elements like B and W are difficult or impossible to measure, because of chemical reactions with graphite. Nevertheless, the technique has been



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applied successfully [1,4], and Zeeman-effect background correction can be used to overcome problems with spectral interferences [1].

The inductively coupled plasma atomic emission spectrometric (ICP-OES) method is usually more sensitive than flame AAS (exceptions to this rule being some of the alkali metals), and can be used for the determination of a larger number of elements, including highly refractory ones. The plasma can be viewed either side-on (radially) or end-on (axially). Detection limits for ICP-OES with radial viewing are generally better than with flame AAS. The detection limits can be improved still further with axial viewing of the plasma. The improvement factor depends on the element and wavelength, but the average improvement factor with axial viewing is 2–3 times, when the same sample introduction system is used [8].

Another approach to improving the detection limit is hydride generation prior to introduction to the AA or AE spectrometer. Nonspectral interferences by transition and noble metals on the generation of hydrides are, however, serious [9], and require pretreatment of the sample to remove the Cu matrix, if hydride generation is to be used [6].

In this study, a sequential ICP atomic emission spectrometer with axially viewed plasma is applied to the determination of trace impurities in Cu reference materials.

Experimental

Instrumental

An Agilent Liberty Series II ICP-OES, with axial viewing of the plasma, was used in this study. An AGM 2 nitrogen purge accessory was used, with an argon flow rate of approx. 15 mL/min⁻¹. A standard glass cyclonic spray chamber and Glass Expansion concentric nebulizer were used throughout, with black-black sample tubing to minimize sample consumption. This sample introduction system was found to provide low sample carry-over, making it suitable for the limited sample volumes available.

Procedure

A 0.5 g aliquot of the sample, obtained in chip form, was weighed into a 100 mL beaker and a 5 mL aliquot of 1:1 nitric acid was added. The flask was then gently warmed to dissolve the Cu completely, and the solution was then diluted to 25 mL with deionized, distilled water. Samples were prepared from the certified reference materials GBW 02111 and GBW 02113 (Office of CRMs, National Research Centre for CRMs, National Institute of Metrology, Beijing 100013, China). Calibration was carried out by matrix matching the standards to the samples. The Cu for matrix matching was obtained as

high-purity chips from a non-commercial source, and was dissolved in HNO₃ by the same procedure as used for the samples. The standards were prepared from BDH standards in dilute HNO₃. Distilled deionized (18 Mohm) water was used for all dilutions.

Choice of Analytical Lines and Background Correction

For most of the elements determined here, the analytical lines used were the same as used in other studies by ICP-OES of bronze [5] and Cu [6] analysis, but there were some differences. Several analytical lines could not be used in the analysis of the Cu CRMs because of spectral interferences from lines of the Cu matrix. With Bi, the 222.825 nm and 223.061 nm lines were not usable because of spectral interferences from nearby broad Cu lines, while the 306.772 nm doublet was also not usable at the low levels of Bi found in the samples because of interference from strong OH lines (306.766 nm and 306.778 nm). These interferences made it necessary to choose the 190.178 nm ionic line for this analysis, rather than the 223.06 nm line used by Segal et al [5]. Several other sensitive lines were also subject to interference by lines from the sample matrix. Where more than one sensitive line was available, as for As, measurements were made on two lines. The analytical lines used here were chosen to offer the best sensitivity while retaining freedom from spectral interference.

Background correction was usually effected by the polynomial plotted background method ("PPB") that is selected as default on the Liberty Series II instrument, but with the line Sb 206.833 nm, off-peak background correction was used to minimize the interference of an OH line, observed with the third (default) grating order on the Liberty Series II. Off-peak background correction was also used for Pb I 283.3 nm

Analytical Conditions

Power	1.2 kW
Plasma gas	15 L/min
Auxiliary gas	1.5 L/min
Spray chamber	Glass cyclonic spray chamber with concentric nebulizer (pressure 240 kPa)
Integration time	3 seconds
Replicates	3
PMT	650 V
Purge gas	AGM-2 accessory was used with argon
Flow rate	10–12 meter units (ca. 2 L/min of Ar)
Pump rate	15 rpm; black-black pump tubing (sample) and blue-blue (drain).

With axial viewing, the preoptics vertical and horizontal positions are set by optimizing on the intensity or SBR of a line. The line used here was the Mn II 257.61 nm.

Results and Discussion

Analysis of Certified Cu Materials

A comparison of measured and certified values of eight elements measured in high-purity copper is given in Table 1. As can be seen, the agreement is very satisfactory for all elements, except for the Fe in GBW 02113, for which an unexpectedly low concentration was found.

Table 1. Analytical Results, Impurities in High-Purity Cu (All Results in Weight Percent)

Axial liberty analytical results, by weight, in high-purity Cu				
Element, line (nm)	GBW 02113		GBW 02114	
	Found %	Actual %	Found %	Actual %
As 188.979	0.0012	0.0013	0.0041	0.0043
As 193.696	0.0015	0.0013	0.0042	0.0043
Bi 190.178	0.0013	0.0013	0.0025	0.0026
Fe 238.204	0.0037	0.0048	0.0085	0.0089
Ni 231.604	0.0170	0.0173	0.0047	0.0050
Pb 283.306	0.0084	0.0083	0.0048	0.0047
Pb 220.353	0.0083	0.0083	0.0047	0.0047
Sb 206.833	0.0019	0.0018	0.0043	0.0042
Sn 189.926	0.0016	0.0017	0.0034	0.0037
Zn 206.200	0.0017	0.0021	0.0043	0.0046

Detection Limits

Because of the limited amount of high-purity Cu that was available for the measurements summarized here, the detection limits were determined for both axially and radially viewing instruments from a detection limit model [10], developed for the Agilent Liberty Series II and validated on several instruments of that series, that uses a combination of the measured SBR and a single blank measurement, the latter sufficing for calculation of RSDB, the relative standard deviation of the blank, thus avoiding the need for repeated measurements of the blank. The detection limit, c_L , is defined [11] as the ratio of the relative standard deviation of the background of the background, RSDB, to the signal-to-background ratio (SBR) per unit concentration of analyte, multiplied by a statistical factor k :

$$c_L = k(0.01)RSDB (c_0/SBR)$$

where RSDB is in %; the constant k is taken here as three.

Results are given in Table 2 for 10 second integrations. High-purity Cu solution was used for measuring the blank signal for each element.

Table 2. Limits of Detection in 2% Cu Solutions (These Values Should be Multiplied by 50 to Obtain the Corresponding Limit of Detection in the Original Solid Sample); 10 Second Integrations

Limits of detection (3-sigma) in high-purity Cu solutions			
Element, line (nm)		Limit of detection in 2% w/v Cu solution, ppb (3-sigma)	
		Axial	Radial
As	188.979	5.6	13.8
Bi	190.178	10.7	20
Fe	238.204	0.43	1.6
Ni	231.604	1.3	5
Pb	283.306	3.5	27
Sb	206.833	3.6	12
Sn	189.926	3.7	13.3
Zn	206.200	0.82	2.7

The detection limits, as measured with the axially viewing Liberty, are better than those found with the radially viewing version, but the signal-to-background advantage of the axially viewing configuration is partly lost when trace elements are measured in Cu matrixes. This is because the increased background, due to Cu, partly offsets the increased analyte signal found with axial viewing, and results in less of an improvement in SBR than in net signal alone – the detection limit being proportional to the ratio of the RSDB to the SBR per unit concentration. The background due to Cu is wavelength-dependent and increases towards the UV. Thus, the detection limit improvement with axial viewing depends on the element and line (as these determine the change in background, and therefore of the SBR) and varied from a factor of ~2 to 3 for the shortest wavelength lines (As 189.0 nm, Sn 189.9 nm, Bi II 190.2 nm) to a factor of ~8 (for Pb 283.3 nm).

Conclusion

The analysis of copper for eight trace elements has been carried out with a sequential ICP emission spectrometer and axial viewing of the plasma. A method based on matrix matching of standards was validated by comparison with results of the analysis of certified reference high-purity copper materials. Detection limits with axial viewing of the plasma were better than with radial viewing by factors of between two and eight, depending on the element.

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